

International literature review on the possibilities of biodiesel production

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Abstract

Continued use of petroleum-based fuels is now widely recognized as unsustainable because of depleting supplies and contribution of these fuels to pollute the environment. The challenge, therefore, is to secure adequate energy supplies at the least possible cost. Over 1.5 trillion barrels of oil equivalent have been produced since Edwin Drake drilled the world's first oil well in 1859. Economic growth is always accompanied by commensurate increase in the transport. The high energy demand in the industrialized world as well as in the domestic sector, and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of limitless duration and smaller environmental impact than the traditional one. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and non-edible oils. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment. The aim of this article is to investigate to hidden possibilities of biodiesel utilisation in Hungary by the review of international literature.

Keywords

diesel fuel · biodiesel

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1 Introduction

The world has been confronted with an energy crisis due to depletion of limited resources of fossil fuel. Continued utilization of petroleum-based fuels is now widely recognized as unsustainable because of depleting supplies and contribution of these fuels to pollute the environment. The challenge is, therefore to secure adequate energy supplies at the least possible cost. Over 1.5 trillion barrels of oil equivalent have been produced since Edwin Drake drilled the world's first oil well in 1859. The world will need that same amount to meet demand in the next 25 years alone. The International Energy Agency has reported in the reference scenario that the world's primary energy need is projected to grow by 55% between 2005 and 2030, at an average annual rate of 1.8% per year. Fossil fuels remain the dominant source of primary energy, accounting for 84% of the overall increase in demand between 2005 and 2030 [1]. Energy and capital have reported that, by 2025, the world's demand for oil will shoot up to 60%, while production capacity would be thrown back to 1985 levels. According to the Energy Information Agency report, petroleum consumption fell by 90,000 barrels per day in 2008–2009. Transportation is one of the fastest growing sectors using 27 % of the primary energy [1]. At the present staggering rates of consumption, the world fossil oil reserve will be exhausted in less than 45 years [2]. Majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gases, and with the exception of hydroelectricity and nuclear energy, these sources are finite and at current usage rates will be consumed shortly [3]. Diesel fuels have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of diesel tractor and pump sets in agricultural sector. Economic growth is always accompanied by commensurate increase in the transport. The high energy demand and pollution problems caused due to the widespread use of fossil fuels make it necessary to develop renewable energy sources. This has stimulated recent interest in alternative sources for petroleum-based fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. One possible alternative to

fossil fuel is the use of oils of plant origin like vegetable oils and non-edible oils. After chemical processes, like transesterification or hydrogenation this alternative diesel fuel can be termed as biodiesel. This fuel is biodegradable and non-toxic and has low emission profiles as compared to petroleum diesel. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment. Chemically the oils/fats consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains. Thus biodiesel refers to lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids. Thus, as far as the exploitation of diesel engines fuelled with diesel/biodiesel blends is well-known, the factfindings of the influence of ethanol additives on engine characteristics presented in the scientific papers are still discussed by many researchers [4]-[17], [53]. These facts have encouraged initiating research on the characteristics of the diesel engine fuelled with blends [8], [14]-[33], [51].

2 Biodiesel

The use of vegetable oils as alternative fuels has been around for 100 years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in his compression ignition engine [30]. He said, *“The use of vegetable oils for engine fuels may seem insignificant today. But such oils may in course of time be as important as petroleum and the coal tar products of the present time”*. However, due to cheap petroleum products, such non-conventional fuels never took off. Oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engine (especially in direct injection engine). The main problem to the use of vegetable oils and especially animal fats are the high viscosity (about 11–17 times higher than diesel fuel), and lower volatilities that cause the formation of deposits in engines due incorrect vaporization characteristics to generate incomplete combustion. Other disadvantages:

- Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices,
- Lubricating problems of injection elements,
- Carbon deposits and oil ring sticking and,
- Thickening or gelling of the lubricating oil as a result of contamination by vegetable oils.

These problems are associated with the large size of the triglyceride molecule and its higher molecular mass and are avoided by modifying the engine less or more according to the conditions of use and the oil involved. The modified engines

built by Elsbett in Germany and Malaysia and Diesel Morten und Geraetebau GmbH (DMS) in Germany and in the USA show a good performance when fuelled with vegetable oils of different composition and grades [3]. The plant oils usually contain free fatty acids, phospholipids, sterols, water, odourants and other impurities. Because of these, the oil cannot be used as fuel directly. To overcome these problems the oil requires slight chemical modification; mainly transesterification, hydrogenation, pyrolysis and emulsification. Among these, the transesterification is the key and foremost important step to produce a cleaner and environmentally safe fuel from vegetable oils. Biodiesel is the monoalkyl ester of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engines. Biodiesel, which is considered as a possible substitute of conventional diesel fuel is commonly composed of fatty acid methyl esters that can be prepared from triglycerides in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics. Due to the more aggressive chemical behaviour of bio-based additives to rubber and plastic parts of the fuel supply system, gaskets and fuel tank, it is recommendable to replace them with those resisting degradation [34].

3 Fuel properties and specification of biodiesel

In view of environmental considerations, biodiesel is considered as ‘carbon neutral’ because all the carbon dioxide (CO₂) released during consumption had been sequestered from the atmosphere for the growth of oil crops. Commercial experience with biodiesel has been very promising. The biggest advantages of biodiesel compared to many other alternative transportation fuels is that it can be used in existing diesel engines without modification, and can be blended with petroleum diesel in required ratio. Biodiesel performs as well as petroleum diesel, while reducing emissions of particulate matter, carbon monoxide (CO), hydrocarbons and oxides of sulphur (SO_x) [35]. Emissions of oxides of nitrogen (NO_x) are, however, higher for biodiesel in many, mainly direct injection engines. Biodiesel virtually eliminates the notorious black soot emissions associated with diesel engines and the total particulate matter emissions are also much lower. Other environmental benefits of biodiesel include the fact that it is highly biodegradable and appear to reduce emissions of air toxics and carcinogens (relative to petroleum diesel). The environmental benefits of 100% and 20% biodiesel blending, in term of pollutants emission reductions are shown in Table 1. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment.

Since biodiesel is produced in quite differently scaled plants from vegetable oils of varying origin and quality, it was necessary to install a standardization of fuel quality to guarantee engine performance without any difficulties. Austria was the first country in the world to define and approve the standards for rapeseed oil methyl esters as diesel fuel. As standardization is a

Tab. 1. Biodiesel vs. diesel emissions.

Emissions	B100, pure biodiesel	B20, mixed biodiesel (20% biodiesel and 80% petroleum diesel)
Regulated emissions (%)		
Total unburned hydrocarbons	-93	-30
Carbon monoxide	-50	-20
Particulate matter	-30	-22
NO _x	+13	+2
Non-regulated emissions (%)		
Sulphates	-100	-20
Polycyclic aromatic hydrocarbons (PAHs)	-80	-13
Nitrated PAHs (NPAHs)	-90	-50
Ozone potential of HC	-50	-10
Life cycle emissions (%)		
Carbon dioxide	-80	
Sulphur dioxide	-100	

Note: (-): Less % of pollutant emission from biodiesel in comparison to 100% petroleum diesel.

(+): More % of pollutant emission from biodiesel in comparison to 100% petroleum diesel, i.e. only in the case of oxides of nitrogen (NO_x).

Source:[50]

prerequisite for successful market introduction and penetration of biodiesel, standards or guidelines for the quality of biodiesel have also been defined in other countries like Germany, Italy, France, the Czech Republic and in the United States. The parameters, which define the quality of biodiesel, can be divided into two groups. One group contains general parameters, which are also used for petroleum based fuel, and the other group describes especially the chemical composition and purity of fatty acid alkyl esters [36]. Table 2 contains the general and Table 3 the oil specific parameters and the corresponding value of fatty acid methyl esters according to the standards of the above mentioned countries.

Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection from the diesel injector. The viscosity of fatty acid methyl esters can reach higher levels and hence it is important to control it within an acceptable level to avoid negative impacts on the fuel injector system performance. Therefore, the viscosity specifications proposed are nearly the same as that of the diesel fuel. Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flash point of biodiesel is higher than that of the petrodiesel, which is safer for transport purposes. Cold filter plugging point (CFPP) of a fuel reflects its cold weather performance. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. Normally either pour point or CFFP are specified. Pour point is the lowest temperature at which the oil specimen can still be moved. French and Italian biodiesel specifications specify pour point whereas others specify CFPP. Cetane number is indicative of its self ignition characteristics. The higher the cetane number are better the ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, driveability, white smoke, noise and emissions of CO and HC. Neutralization number is specified to ensure proper ageing properties of the fuel and/or

a good manufacturing process. It reflects the presence of free fatty acids or acids used in manufacture of biodiesel and also the degradation of biodiesel due to thermal effects. Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel. Conradsons Carbon Residue for biodiesel is more important than for diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities. The presence of high level of alcohol in biodiesel causes accelerated deterioration of natural rubber seals and gaskets. Therefore control of alcohol content is required. Biodiesel fuel mainly consists of fatty acid alkyl esters and its quantities are specified according to the specifications of various countries. The presence of mono-di- and triglycerides cause engine problems like fuel filter plugging affecting the fuel properties and are specified in most of the biodiesel standards.

4 Biodiesel production from used cooking oil

In most parts of the world edible oils are used in frying pans or fryers and after a variable time of use are discarded.. At present there is no systematic method of processing used oils from households and most of the used oil is mostly disposed of through home drains and ends up in wastewaters that are then discharged to surface waters, leading to water pollution. Moreover, more than 80% of the oil is consumed at home; the control of this disposal behavior becomes a huge problem because of the large volumes involved. Despite the gains made in biodiesel production techniques, the cost of biodiesel is still higher than petroleum-based diesel and this has been a major barrier to its commercialization. One of the ways widely accepted for reducing the cost focuses on minimizing the raw material cost. The use of waste cooking oil instead of virgin (neat) oil to produce biodiesel has been found to be an effective way to reduce the raw material cost. Hence reusing of the waste cooking oil has both the benefit of producing an environmentally benign fuel

Tab. 2. General parameters of the quality of biodiesel

Parameters	Austria (ON)	Czech (CSN)	Republic	France (journal official)	Germany (DIN)	Italy (UNI)	USA (ASTM)
Density at 15°C [g/cm ³]	0.85-0.89	0.87-0.89		0.87-0.89	0.875-0.89	0.86-0.90	-
Viscosity at 40 [mm ² /s]	3.5-5.0	3.5-5.0		3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0
Flash point [°C]	100	110		100	110	100	130
CFPP [°C]	0/-5	-5		-	0-10/-20	-	-
Pour point [°C]	-	-		-10	-	0/-5	-
Cetane number	≥ 49	≥ 48		≥ 49	≥ 49	-	≥ 47
Neutralization number [mgKOH/g]	≤ 0.8	≤ 0.5		≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.8
Conradson carbon residue [%]	0.05	0.05		-	0.05	-	0.05

Source:[52]

Tab. 3. Vegetable oil specific parameters for the quality of biodiesel

Parameters	Austria (ON)	Czech (CSN)	Republic	France (journal official)	Germany (DIN)	Italy (UNI)	USA (ASTM)
Methanol/ethanol (% mass)	≤ 0.2	-		≤ 0.1	≤ 0.3	≤ 0.2	-
Ester content (% mass)	-	-		≥ 96.5	-	≥ 98	-
Monoglyceride (% mass)	-	-		≤ 0.8	≤ 0.8	≤ 0.8	-
Diglyceride (% mass)	-	-		≤ 0.2	≤ 0.4	≤ 0.2	-
Triglyceride (% mass)	-	-		≤ 0.2	≤ 0.4	≤ 0.1	-
Free glycerol (% mass)	≤ 0.02	≤ 0.02		≤ 0.02	≤ 0.02	≤ 0.05	≤ 0.02
Total glycerol (% mass)	≤ 0.24	≤ 0.24		≤ 0.25	≤ 0.25	-	≤ 0.24
Iodine number	≤ 120	-		≤ 115	≤ 115	-	-

Source:[52]

and solving the problem of waste oil disposal. The methods of production of biodiesel from used cooking oil do not differ from the conventional transesterification process using alkaline, acidic, and enzymatic catalysts. Depending on the undesirable compounds (especially FFA and water), each catalyst has its advantages and disadvantages. These used frying oils have different properties from those of refined and crude vegetable oils. The presence of heat and water accelerates the hydrolysis of triglycerides and increases the content of free fatty acids (FFA) in the oil [37]. The FFA and water content have significant negative effects on the transesterification reaction [38]. They also interfere with the separation of fatty acid esters and glycerol. Especially, the viscosity of the oil increases considerably, because of the formation of dimeric and polymeric acids and glycerides in used cooking oils. Molecular mass and iodine values decrease while saponification value and density increase [37]-[39]. A typical schematic diagram for the production of biodiesel from used cooking oil is shown in Fig. 1.

5 Microalgae are emerging feedstock for biodiesel production

Algae are very important from an ecological point of view. Algae are the food source for many animals and belonging to the bottom of the food chain; moreover, they are the principle producers of oxygen on earth. Their important role as food source is due to the content of minerals, vitamins and oils, rich in polyunsaturated fatty acids (PUFAs). PUFAs such as α -linolenic, eicosapentaenoic and docosaesaenoic acids, belong to the ν -3 group

[40]. Algae having the ability to synthesize TAGs are considered as a second generation feedstock for production of biofuels, specifically biodiesel. The potential value of microalgal photosynthesis to produce biofuels is widely recognized [41]-[44]. The advantages of microalgae over higher plants as a source of transportation biofuels are numerous:

- 1 Microalgae synthesize and accumulate large quantities of neutral lipids/oil [20–50% dry cell weight (DCW)] and grow at high rates (e.g. 1–3 doublings/day).
- 2 Oil yield per area of microalgae cultures could greatly exceed the yield of best oilseed crops.
- 3 Microalgae can be cultivated in saline/brackish water/coastal seawater on non-arable land, and do not compete for resources with conventional agriculture.
- 4 Microalgae tolerate marginal lands (e.g. desert, arid and semi-arid lands) that are not suitable for conventional agriculture.
- 5 Microalgae utilize nitrogen and phosphorus from a variety of wastewater sources (e.g. agricultural run-off, concentrated animal feed operations, and industrial and municipal wastewaters), providing the additional benefit of wastewater bioremediation.
- 6 Microalgae sequester CO₂ from flue gases emitted from fossil fuel-fired power plants and other sources, thereby reducing emissions of a major greenhouse gas. 1 kg of algal biomass requires about 1.8 kg of CO₂ [43].

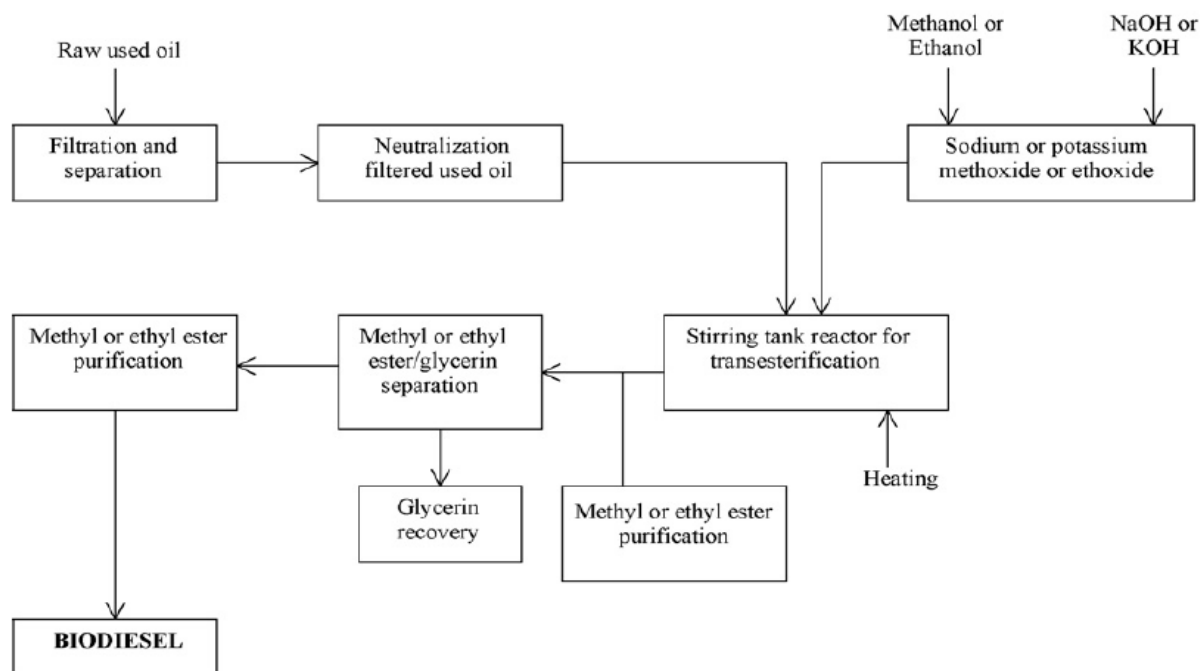


Fig. 1. Schematic flow diagram of the bio-diesel production from used cooking oil *source: [54]*

7 Microalgae produce value-added co-products or by-products (e.g. biopolymers, proteins, polysaccharides, pigments, animal feed and fertilizer) and does not need herbicide and pesticide.

8 Microalgae grow in suitable culture vessels (photobioreactors) throughout the year with higher annual biomass productivity on an area basis.

Microalgae can provide several different types of renewable biofuels. These include methane produced by anaerobic digestion of the algal biomass biodiesel derived from microalgal oil, [45]-[46] and photobiologically produced biohydrogen [47]-[48]. The idea of using microalgae as a source of fuel is not new but it is now being taken seriously because of the rising price of petroleum and, more significantly, the emerging concern about global warming that is associated with burning of fossil fuels [46]. Using microalgae to produce biodiesel will not compromise production of food, fodder and other products derived from crops. A comparison of some sources of crop oil is given in Table 4.

In view of Table 4, microalgae appear to be the only source of biodiesel that has the potential to completely displace fossil diesel. Oil content in microalgae can exceed 80% by weight of dry biomass [45-46, 51]. Oil levels of 20–50% are quite common. Oil productivity, that is the mass of oil produced per unit volume of the microalgal broth per day, depends on the algal growth rate and the oil content of the biomass. Using microalgae also has the potential to avoid the controversies around the alternative fuel goals of the EU (competition for arable land, water footprint, etc.) [55].

Tab. 4. Comparison of algae with different crops for biofuel.

Source	Liter of oil per hectare per year
Algae	46700-187000
Oil palm	5940
Coconut	2685
Jatropha	1936
Rapeseed/Canola	1188
Peanut	1057
Sunflower	954
Safflower	776
Soybeans	449
Hemp	365
Corn	168

Source: [50]

6 Conclusion

Under the existing EU standards, petrol and diesel shall contain biocomponents; moreover, it is required that the content of such biocomponents shall be continuously increased. The use of alternative fuels or their components is also promoted. Alternative fuels are defined as any materials or substances produced from renewable sources that can substitute petroleum fuels or any part thereof and are used for the purposes of economy and with a view to reducing pollution caused by transport. The fuels of biological origin mixed with conventional fuels or added thereto as individual components are the most frequently used type of alternative fuels.

The quality of biodiesel is most important from an engine point of view and various standards have been specified to check the quality. At the present moment, biofuels are derived from food crops such as sugarcane, sugar beet, maize

(corn), sorghum, rapeseed, sunflower, soybean and palm, although other forms of biomass can be used, and may be preferable. The most significant concern is the inefficiency and sustainability of these first generation biofuels. In contrast, the second generation biofuels are derived from non-food feedstock. They are extracted from microalgae and other microbial sources, lignocellulosic biomass, rice straw and bioethers, and are a better option for addressing the food and energy security and environmental concerns [42,56].

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